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LARGE PLATE CdTe SYNTHESIS BY SEALED
VESSEL TRANSPORT

A. R. HILTON, PRINCIPAL INVESTIGATOR
(214) 494-5624

QUARTERLY TECHNICAL REPORT NO. 6

REPORT PERIOD: APRIL 1 - JUNE 30, 1983

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AMORPHOUS MATERIALS, INC.

AMTIR

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214/494-5624 – 271-8613

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The sixth quarterly technical report for the program to grow large plates of high purity CdTe in a sealed system covers the period April 1 - June 30, 1983. The process to grow 8" diameter plates of CdTe high in purity with large grain sizes has been developed. Evaluation results from other workers have confirmed the purity and high resistivity of the resultant materials. Attempts to confirm optical homogeneity using an MTF test failed because of our inablility to polish the material flat. A method for generating 2" diameter disks from the plates was developed. Results from the evaluation of 2" disks are presented. The first attempt

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SUMMARY

The goal of this program is to use vapor growth to form polycrystalline plates of cadmium telluride (CdTe) 6", 8" and 10" in diameter. The resultant material will be evaluated as substrates for mercury-cadmium-telluride (HgCdTe) growth and as an infrared optical material. Late in the program, mercury vapor will be used in an attempt to grow HgCdTe layers on the large area CdTe plates.

Previous workers have grown large plates of CdTe 6" in diameter transporting the vapor using an inert gas. The starting material was pre-compound. The method to be used in this program was to compound the material and transport the vapor through a filter into the casting chamber for growth in one operation under vacuum. Solid state recrystallization carried out at high temperatures over a long period of time will produce the desired large grain structure.

Results reported in the first three quarters demonstrated the initial process concept was impractical. Vapor transport of compounded CdTe in a sealed evacuated system was too unpredictable. High temperatures coupled with the presence of cadmium oxide caused a high percentage of quartz failures. Program goals could not be reached with the original process approach. The decision was made to convert to a three chamber quartz system in which the cadmium and tellurium vapors entered the plate chamber from separate tubes.

The new process approach was used ten times to produce 6" diameter plates from a stoichiometric melt. Plates weighing almost 2Kgms and possessing the required large grain structure

resulted. However, a void region was found to occur between the faces of the plate each time. Growth from solution was used to eliminate this problem. A plate was grown with grains running from the bottom face to the top face from a solution of approximately Cd45 Te55. Total process time was about 72 hours.

The process was applied to the growth of 8" diameter plates successfully. Some changes had to be made particularly with regards to the sequence of reactant distillation. Plates with large grains several inches in area have been grown. Thickness of material is 0.5" or less with the weight of useful material reaching up to 2Kgms. The material has been found to be high purity by emission spectrographic analysis, high resistivity and to exhibit no or little free carrier absorption in the infrared. Disks may be generated from the plate by cutting out squares followed by edging. Attempts to verify the optical homogeneity using an MTF test failed because of an inability to polish pieces flat. The first attempt to grow a 10" diameter plate failed because of a crack which formed in one of the quartz chambers.

Next quarter, efforts to grow 10" diameter plates will resume. Material will be cut from the plates, evaluated and compared to material from 8" plates. A new wire saw has been purchased to use for cutting thin substrates from large grain 2" diameter disks. The substrates will be sent to other groups for evaluation. Attempts will also be made to grow mercury-cadmium-telluride layers on our substrates ourselves.

I INTRODUCTION

A crucial problem in the volume production of U. S. Government FLIR systems is the availability of mercury-cadmium-telluride (HgCdTe) detector arrays. Certainly fabrication of the arrays is difficult but the major problem is the availability of high quality detector material. The production of bulk HgCdTe alloy is a slow, difficult low yield process. The preferred method to produce detector materials is to grow HgCdTe layers epitaxially on a high quality cadmium telluride (CdTe) substrate. However, the availability of high quality Cd Te is also limited. Part of the reason for the shortage is that the conventional method for preparing CdTe crystals is to slowly (0.1"/hour) zone refine small diameter (1") crystals using the Stockbarger technique. The purpose of this program will be to develop an alternative approach.

Large plates of high purity large grain cadmium telluride will be grown from the vapor in a sealed system. Cadmium telluride will be compounded from the elements and sublimed through a filter into a separate growth chamber 6", 8" or 10" in diameter. Grain size will be increased by solid state recrystallization. Material thus produced will be evaluated regarding purity, optical homogeneity and suitability as substrates for HgCdTe growth. Attempts will be made to grow HgCdTe layers by mercury vapor deposited on large area plates insitu.

II. VAPOR GROWTH OF CADMIUM TELLURIDE

A. General

Cadmium telluride is formed from the group II element

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cadmium and the group VI element tellurium. All II-VI com-
pounds, as they are called, are difficult to grow because of
their high melting points and the fact that both constituent
elements are volatile. An appreciable vapor pressure exists
for each element at the solid melting point which leads to
complications for melt growth. For the same reason, vapor
growth of the solid becomes attractive.

Solid CdTe may be grown from the vapor at temperatures
considerably below its melting point, $1097^{\circ}C$, according to
the following equation:

$$Cd\ (g) + \tfrac{1}{2}\ Te_2(g) \rightleftharpoons CdTe\ (s)$$
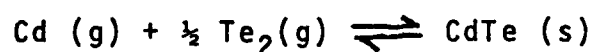
Where: g signifies gas or vapor

s signifies solid

The reaction as written is reversible which indicates
that solid CdTe will sublime or vaporize into its constituent
elements. Thus, the source of Cd or Te_2 gas may be either the
pure heated elements or a heated source of pre-compounded CdTe
solid.

The quality of the CdTe grown from the vapor (or melt)
depends upon maintaining the exact ratio of 1:1 between the
cadmium and tellurium atoms. The pressure of cadmium vapor
(pCd) and the pressure of tellurium vapor (pTe_2) in equili-
brium over solid CdTe at the growth temperature is very cri-
tical and a function of temperature. Deviations from stoich-
iometry will occur if the ratios are not closely controlled.
Supplying the vapors from pure elemental sources heated sep-
arately and mixed together at the reaction sight is not too
accurate. Even the use of inert carrier gasses does not im-
prove the situation to any great extent. Sublimation of pre-
compounded CdTe follo ed by   moval of the vapor to the reac-
tion sight is far more curate. The compounded material may

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be weighed to an accuracy of 0.1% or better. The accuracy of the ratios may be maintained through direct sublimation in a closed system or through use of an inert carrier gas in a flowing system.

One quality criteria not mentioned thus far is crystal-linity. In melt growth, crystals of one single grain may be grown provided that a seed is used and growth rates are very slow. Such restrictions are also the prime limitation relative to diameter of the crystal. In vapor growth, crystals are grown on other crystal surfaces of the same or similar struc-ture, or they grow on an amorphous substrate with spontaneous nucleation and growth occuring over the entire surface. The first case may produce single crystals provided that growth conditions are carefully controlled. The latter method may produce large grain material provided high growth temperatures are maintained over long periods of time.

B. Previous Work

The first extensive investigation of the preparation of CdTe was carried out by D. de Nobel [1] of Phillips. The re-sults published in 1959 details the thermodynamic properties, optical, electrical and semiconducting properties of the ma-terials. The liquidus-solidus curve and related pressure-temperature studies have served as the basis for melt growth of CdTe over the years. Discussions related to melt growth will not be repeated here only as they are relative to vapor growth.

L. R. Shiozawa and co workers at Gould (now Cleveland Crystal Laboratories) carried out an extensive investigation

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beginning in the late 1960's concerning the vapor growth of II-VI compounds generally [2] and cadmium telluride [3] specifically. Diagrams from their papers will be used to discuss the problems involved in vapor growth of cadmium telluride.

Figure 1 shows the simple binary phase diagram of the Cd-Te system [2]. The diagram indicates a single compound is formed, CdTe, which has a congruent melting point of $1092^{\circ}C$. The term "congruent melting point" indicates that except at perfect stoichiometry, below the $1092^{\circ}C$ melting point, both Cd rich and Te rich liquids exist in equilibrium with pure CdTe. The point is better illustrated in the diagram [4] shown in figure 2. Only in a vary narrow range of stoichiometric ratios does the pure CdTe and its equilibrium vapor pressure exist. The range is less than one part per hundred thousand or 0.001 percent. Minimum vapor pressure at all temperature exist along this line. Equilibrium vapor pressure would be exactly in the right ratio. However, considering the accuracy required, it is more likely that the solid cadmium telluride would be either Cd rich or Te rich. Vapors above the solid would reflect this fact and be larger than those above exactly stoichiometric material.

The pressure of cadmium at the cadmium rich boundry stability field as a function of temperature [2] is shown in figure 3. The tellurium rich [2] is shown in figure 4. In both diagrams, the data is compared to the pressure for the pure element, P Cd (1) and P Te2 (1). For the low temperature, the measured values are very close to those for the pure liquid or close to those corrected according to RAOULT's Law. RAOULT'S law states the vapor pressure of a component is lowered by its atomic fraction in a liquid mixture:
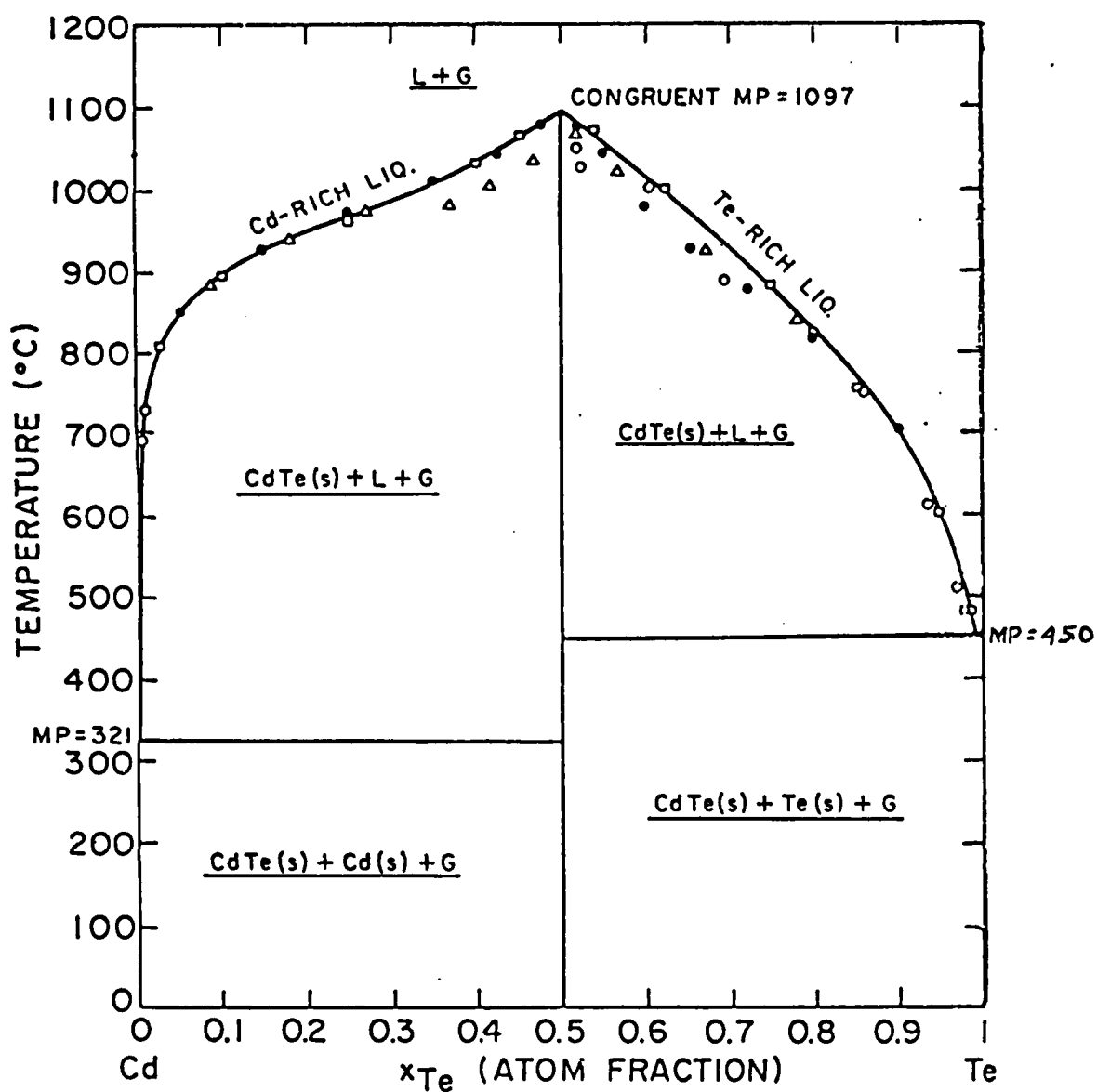
FIG. 1. PHASE DIAGRAM OF THE Cd-Te SYSTEM.
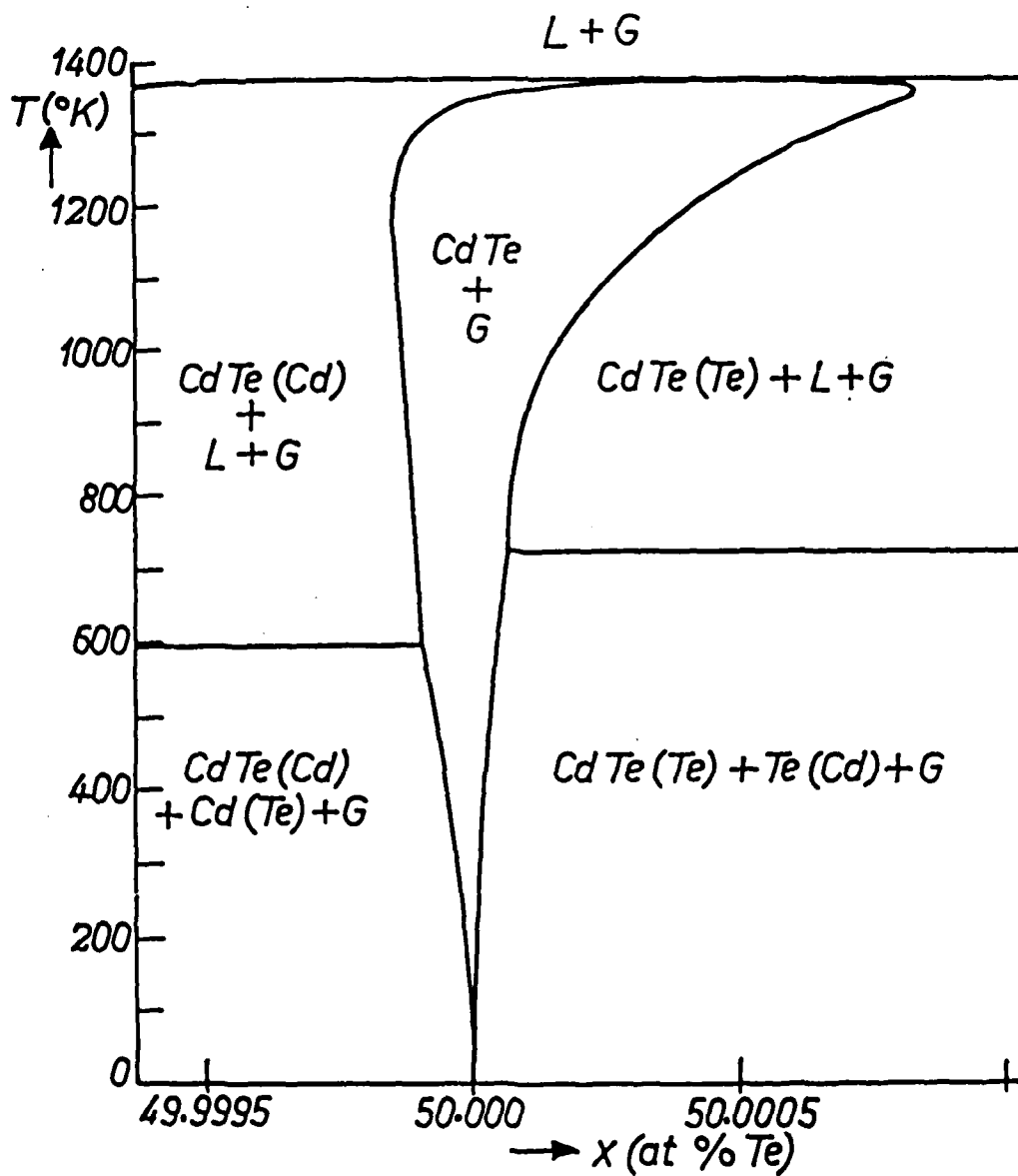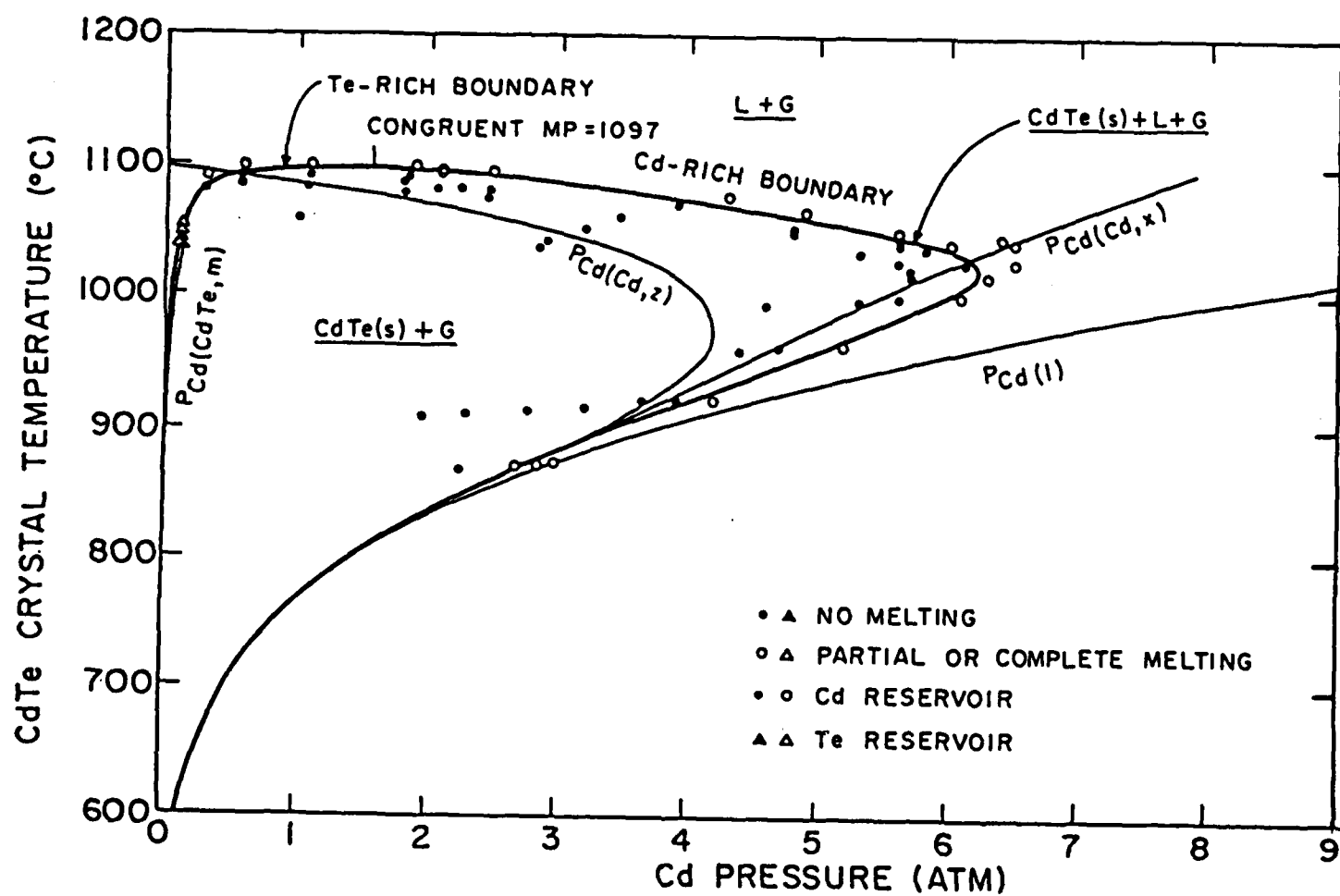
FIG. 2.   SOLID STABILITY FIELD OF CdTe.

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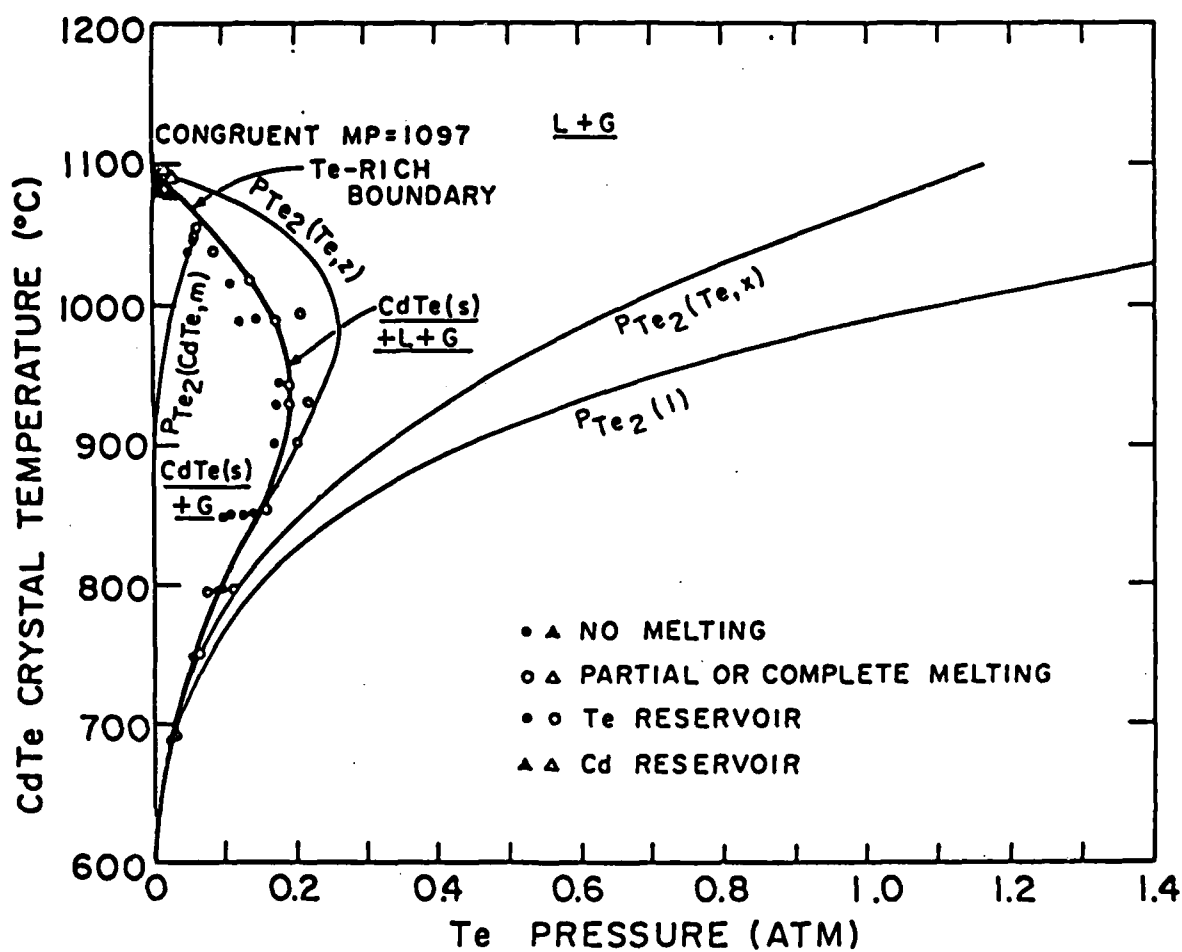FIG. 3. Cd-RICH BOUNDARY OF THE SOLID CdTe STABILITY FIELD. (PRESSURE-TEMPERATURE PROJECTION.)

FIG. 4. Te-RICH BOUNDARY OF THE SOLID CdTe STABILITY FIELD. (PRESSURE-TEMPERATURE PROJECTION.)

P Cd   =   x   P Cd (1)

Where   P Cd is the pressure of cadmium above
         the melt
         P Cd (1) is the pressure of pure cadmium
         at the temperature of measurement
         X   is the atomic fraction of cadmium in the
         melt.

A similar statement may be made for the pressure of tellu-
rium. The calculated curves using X are a simple application
of RAOULT'S law. Those using the Z subscript indicates that
association between the atoms in the liquid are taken into
account. The curves labeled with the M subscript correspond
to the minimum pressure conditions which exist with only pure
Cd Te solid present.

The diagrams indicate that the pressure of cadmium may
become very large, 4-6 atmospheres, around $1000^{\circ}C$ when com-
pounding cadmium telluride. The pressure at the congruent
melting point, $1092\ ^{\circ}C$, is about 0.65 atmospheres. The vapor
pressure of tellurium is quite low throughout the compound-
ing range. The trick to compounding without an explosion is
to stay close to the perfect stoichiometry point and allow
time for the liquid phases to become small in quantity. The
trick in vapor growth is to be sure that the subliming ma-
terial is near the stoichiometric ratio so that the resulting
vapors are close to the proper ratio. Maintenance of the pro-
per ratio during vapor growth is complicated by the fact that
tellurium exists as a diatomic gas, Te2. The effusion rate
for a gas is inversly proportional to the square root of its
molecular weight and directly proportional to its pressure.
Therefore, for CdTe sublimation, we find the effusion ratios
to be [2]

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$$R\ Cd/R\ Te_2 = (PCd/PTe_2)\ (MW\ Te_2/MW\ Cd)^{1/2}$$

Where   R is effusion rate

                 P is pressure

                 MW is molecular weight

Even though the vapor starts out at the perfect 2/1 ratio, the cadmium atoms move faster changing the effusing gas mixture ratio. For Cd Te, the ratio becomes 1.33 instead of 2. Build up of the excess component may limit the deposition rate in a sealed system where equilibrium type conditions may be established. The equilibrium constant is given by:

$$K\ Cd\ Te(s) = (PCd)\ (P\ Te_2)^{1/2}$$

The build up of one component over the other shifts the equilibrium and suppresses further sublimation. Some have used capillary tubes to allow the excess component build up in the vicinity of the source to be pumped away or eliminated. Others have used a carrier gas to carry the subliming vapors, with perfect ratios, to the deposition surface.

C. Vapor Growth of CdTe Plates

Shiozawa [3] and co-workers at Gould used physical vapor deposition (PVD) to grow CdTe plates up to 6" in diameter. Figure 5 illustrates the type of systems used. Pre-compounded CdTe was sublimed from the hot zone of a furnace to a slightly cooler zone. Best results were obtained when growth temperatures of 1000-1050°C were used. Recrystallization was allowed to occur over periods up to 400 hours (17 days).

Figure 6 illustrates the type of grain sizes which were obtained. Growth and recrystallization at 950°C produced small grains. Fast deposition and short growth periods even at the high temperatures produced plates with samll grains and voids.
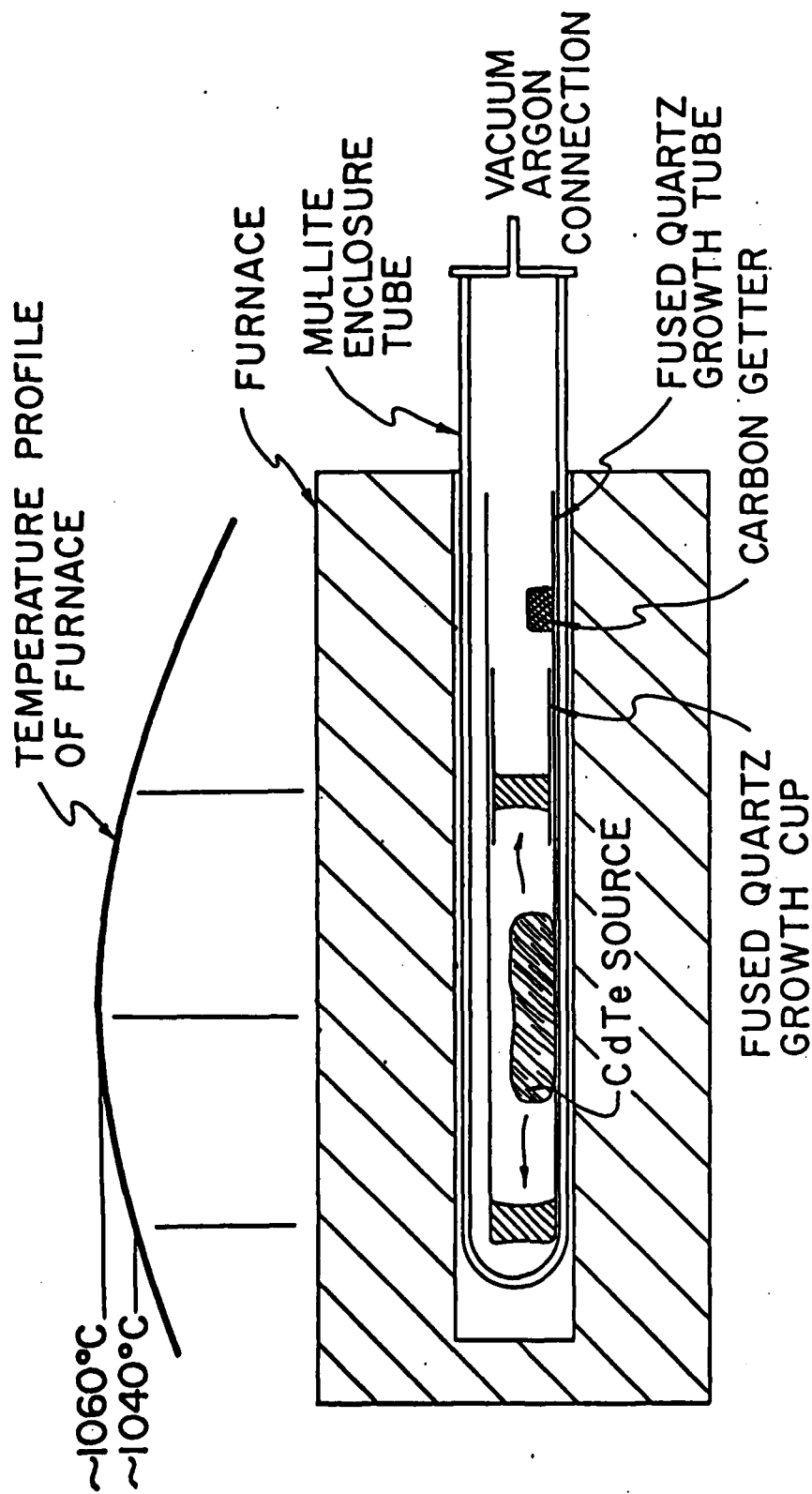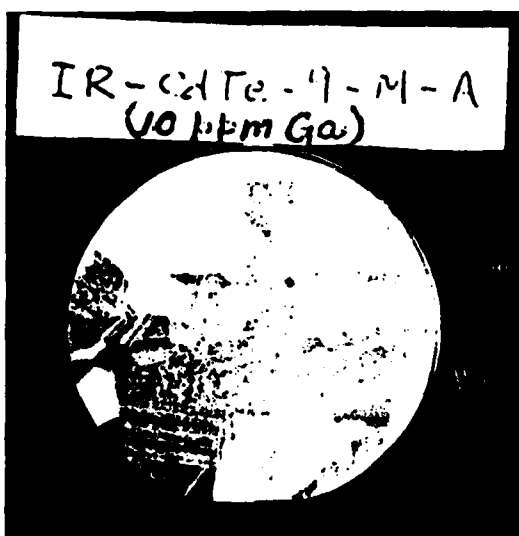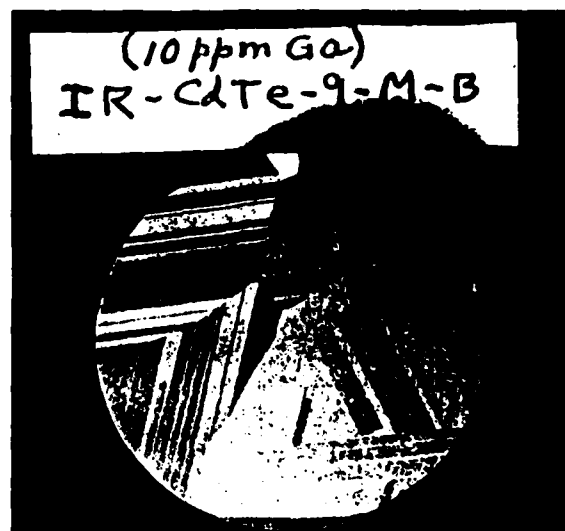
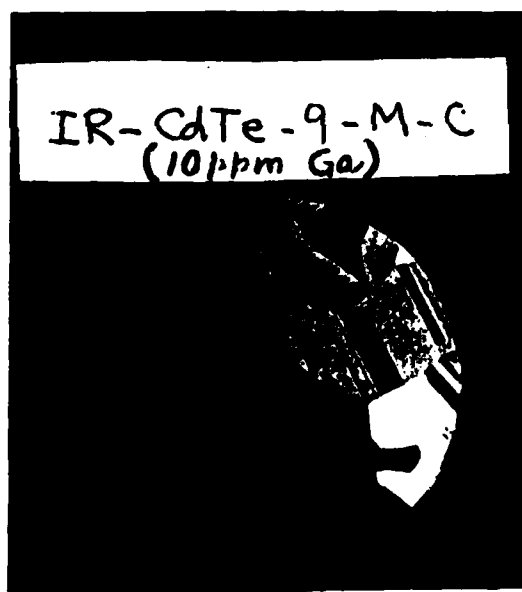FIG. 5. HORIZONTAL SYSTEM FOR CRYSTAL GROWTH BY GRAIN GROWTH
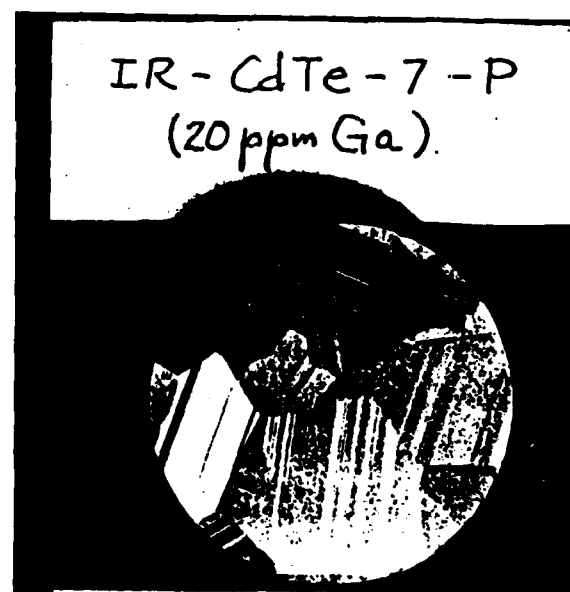
FIG. 6. Lapped Surfaces of CdTe Window Blanks Highlighting Grain
and Twin Patterns.

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The systems were operated semi-sealed. Argon gas was used as a carrier. Pressures up to 1 atmosphere was used but 180 mm, the vapor pressure of stoichiometric Cd Te at 1050°C, was the preferred pressure. Later versions of the system used graphite parts to minimize the effects of air leaks. Also, inert gas was flowed through the furnace to protect the graphite components.

Plates thus produced were heat treated with both Te_2 and Cd vapors at temperatures of $700-800^{o}$C. Treatments were alternated and lasted 1-5 days. Measured absorption at 10.6μm was $0.001-0.002$ cm^{-1}. The effect of heat treating on the infrared transmission of one of their CdTe plates is shown in figure 7. From the transmission for Cd treatment alone, one can see that dual treatment is necessary. After treating with Te_2 vapor, almost theoretical transmission was obtained.

III APPLICATION OF THE AMTIR METHOD TO THE GROWTH OF CdTe

A. Preparation of AMTIR-1 glass

A simplified diagram depicting the glass compounding and casting process developed by Amorphous Materials, Inc. to produce AMTIR-1, is shown in figure 8. A high purity quartz container is placed in a dual zone resistive heated furnace. Zone 1 contains the round empty chamber which will serve later in the process as the casting mold. Zone 2 contains the glass compounding chamber. The process employed at Amorphous Materials combines all three glass processes (element purifications, compounding the glass and casting the plate) into a single continuous process.
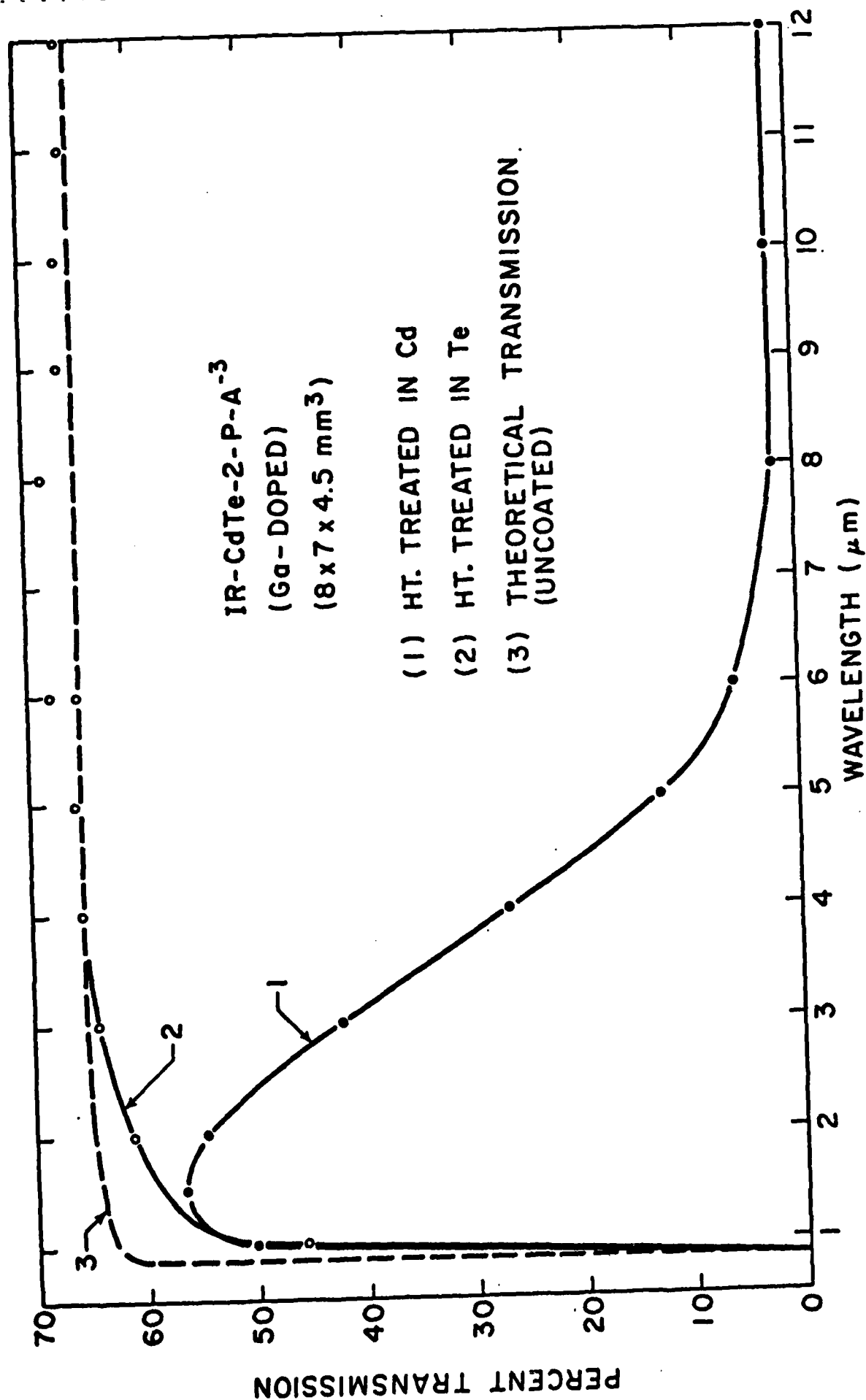
FIG. 7. OPTICAL TRANSMISSION OF Ga-DOPED CdTe

IR-CdTe-2-P-A-3
(Ga-DOPED)
(8 x 7 x 4.5 mm^3)

(1) HT. TREATED IN Cd
(2) HT. TREATED IN Te
(3) THEORETICAL TRANSMISSION.
(UNCOATED)

WAVELENGTH (μm)

PERCENT TRANSMISSION

FIGURE 8. GLASS PROCESS DIAGRAM
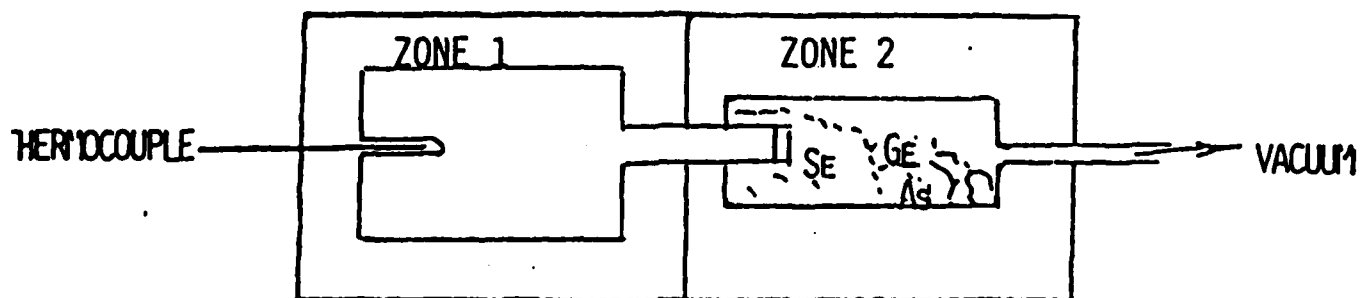
PURIFICATION
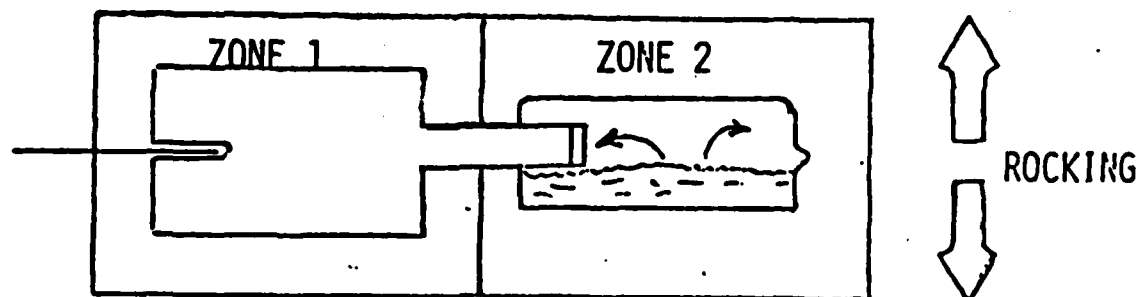
COMPOUNDING
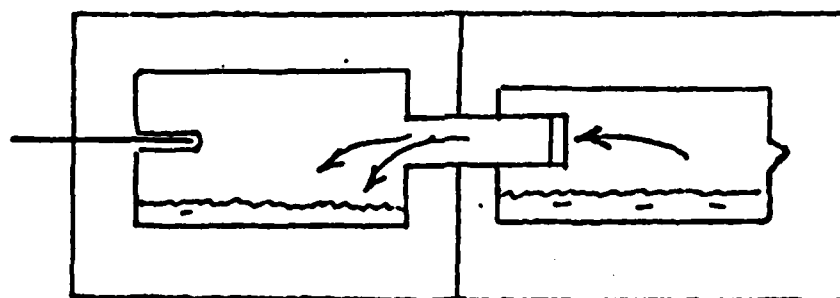
DISTILLATION

CASTING

17
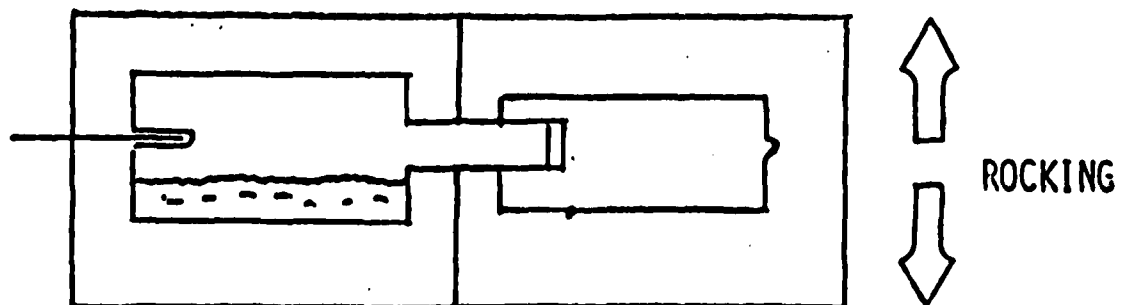
In the first step, both chambers are evacuated and heated to remove moisture. A small amount of aluminum wire is added to the elements to act as a getter of oxides in the molten glass. After several hours, the chamber is sealed off while still under vacuum by heating and collapsing the pumping tube. The furnace is closed and need not be opened again until the glass is quenched.

The temperature is raised in both chambers while rocking the furnace. The casting chamber is heated to prevent premature transfer of the elements from the compounding chamber. The furnace is rocked for several hours to insure that all the elements have reacted properly and are uniformly mixed.

Rocking is stopped and the glass casting chamber cooled to allow transfer of the compounded glass into the casting chamber. Distillation occurs through a porous quartz filter which removes all particulate matter. The distillation generally takes 12-15 hours. The amount of material passed through the frit varies depending upon diameter and thickness. A 6" diameter plate 2" thick requires about 4Kgms of glass while a 8" diameter plate 2" thick requires 7Kgms of material. It is interesting to note that the purity of the finished material improves with quantity prepared. The total amount of impurities from quartz walls, vacuum system, etc. remains constant while the ending concentration decreases with increase in mass. The distilled glass is mixed by rocking. The glass is then allowed to cool while rocking down to the casting temperature range. Rocking is stopped and the furnace leveled up. The glass is rapidly cooled using compressed air to the anneal range $370^{\circ}C$. The glass is annealed 6-8 hours before being allowed to cool to room temperature.

AMTIR-1 glass is compounded in very unique and valuable high purity quartz containers. Casting chambers 6", 8" and 10" in diameter are routinely prepared. Methods have been worked out to open the chambers with a diamond saw so that the cast plate may be removed without breaking. The chambers are cleaned up and resealed for reuse. The compounding tubes are not saved. The impurities within the high purity beginning reactants are left behind during the distillation. The residues are sometimes quite large indicating the effectiveness of the method in preparing high purity solid materials.

B. Modification for Vapor Growth of Cd Te

The temperature range involved in cadmium telluride compounding and solid state recrystallization is 1050-1100°C, well above the compounding temperature used for AMTIR-1. However, the furnaces are of sufficient caliber to reach and maintain these temperatures continuously. Times involved are much longer. From start to finish the AMTIR-1 process requires 48 hours to produce a plate. High quality cadmium telluride grown from the vapor with solid state recrystallization (grain growth method) requires 300-400 hours (12-17 days) to produce good quality material 1" thick[3]. For a 6" diameter plate, 2700gms of cadmium telluride would be grown. Considering all these factors, the procedure carried out would be as follows:

1. The correct amounts of high purity cadmium and tellurium will be weighed out and placed in the compounding chamber as before. For a 6" plate, about 2700 grams will be required. High purity aluminum wire will be added (10-20ppm) to serve as an oxide getter. The casting chamber may need to be carbon coated using graphite formed from the pyrolysis of acetone.

2. The compounding and casting chambers will be heated to 200°C to remove moisture and the chamber will be tipped off.

3. The casting chamber will be heated to 1100°C. The compounding side will be heated to the boiling point of cadmium (765°C) and rocking begun. Over a period of hours, the temperature will be increased to 1100°C while rocking to insure complete compounding of the cadmium telluride.

4. Rocking will cease and material transfer begun. The casting chamber side will be reduced to a temperature of 1000-1050°C to bring about transfer of material to the plate side. The high temperature will be maintained so that grain growth will be a continuous process. Particulate matter and oxide impurities will remain behind in the compounding chamber. The time involved may be as long as 10-15 days.

5. After completion of the run, the cadmium telluride plate will be removed from the chamber using a horizontal glass saw as is done for AMTIR plates.

C. Program Objectives

A large diameter, thick, high purity, large grain plate of cadmium telluride will be formed. Individual large grains 1-4cm^3 in volume will be visible in the surface of the plate after lapping and light etching. Evaluation and treatment of the plate depends upon the desired use.

First emphasis of the program will be to establish the growth parameters using 6" diameter chambers. Purity of resultant material will be verified by chemical analysis. Electrical, mechanical and optical evaluation techniques will be

used where appropriate. After growth parameters are estab-
lished, scale up for 8" diameter and 10" diameter plates will
occur.

Substrates will be cut out of 6", 8" and 10" diameter plates
for evaluation for HgCdTe epitaxial growth. Disks 2" in dia-
meter and 0.1" thick will be prepared for evaluation by groups
designated by DARPA.

Disks 2"D x 0.25" thick will be prepared for optical homo-
geneity verification. The disks will be polished flat and pa-
ralled in order to carry out MTF based image spoiling tests.
Additionally, lenses will be fabricated for evaluation in the
U. S. Army small imager FLIR common Module.

The last goal of the program will be to grow large area
HgCdTe layers insitu. Mercury vapor will be admitted into
the 6", 8" and 10" diameter CdTe growth chambers in an attempt
to produce layer growth of the right composition.

D. Vapor Growth Results

The results obtained in 14 attempts to prepare CdTe plates using a stoichiometric vapor approach was discussed in detail in Technical Report No. 2. The major difficulties encountered are summarized below:

1. Numerous quartz failures occured probably due to the attack of cadmium vapor at high temperatures and moderate pressures.

2. Formation of solid CdTe in the filters caused plugging. The use of filters had to be abandoned early to aid attempts to transfer the stoichiometric material from the compounding chamber to plate chamber.

3. Sublimation of stoichiometric material in a vacuum system is difficult to control and unpredictable. Excess of one component relative to another will shift equilibrium conditons.

4. Deposition does not always occur where desired.

5. Analytical results reported in technical Report No. 3 did not demonstrate a purity improvement over the reactants. Filters were not used.

6. Trying to pass Cd and Te vapors through the same entrance at the same time to the plate chamber is the cause of major problems.

E. Vapor-Melt Growth Method

The conclusion reached from the vapor growth results
was that the Cd and Te vapors could not enter the plate
chamber through the same entrance. A three chamber zone
approach would be required if the program goals were to
be met. A diagram depicting the modification of the AMTIR
method is shown in figure 9.

The elements are melted and purified while being
pumped from both ends. After this step is completed and
the chambers sealed, one element is transferred into the
plate chamber and condensed as a liquid. In this case,
Te is transferred first. Condensation as a liquid in the
bottom of the chamber insures CdTe plate growth will occur
where it is most desired. Notice the plate chamber is wrapped
with quartz wool insulation to insure uniform temperature.

The second step involves compounding CdTe by transfer-
ring Cd vapor into the chamber. After the melt is compounded,
air may be blown on the bottom of the chamber to promote
crystal growth from the center and the bottom of the melt.
The procedure, equipment used and early results were reported
in Technical Report No. 3.

FIGURE 9. THREE ZONE MELT GROWTH PROCESS

ZONE 1   ZONE 2   ZONE 3

VACUUM
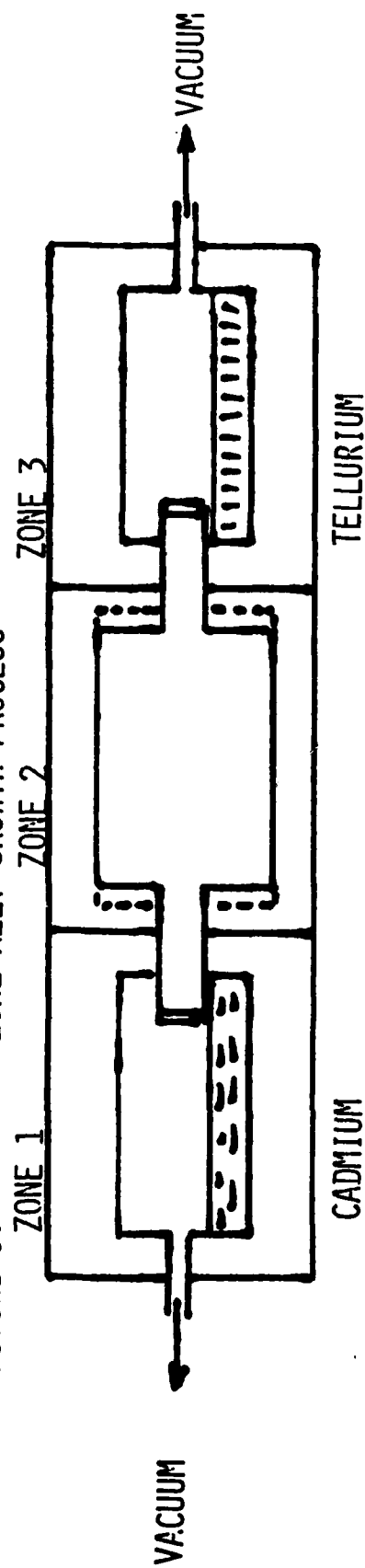
CADMIUM   TELLURIUM

REACTANT PURIFICATION

TELLURIUM TRANSFER

INSULATION

AIR   CADMIUM TELLURIDE GROWTH

VACUUM

24
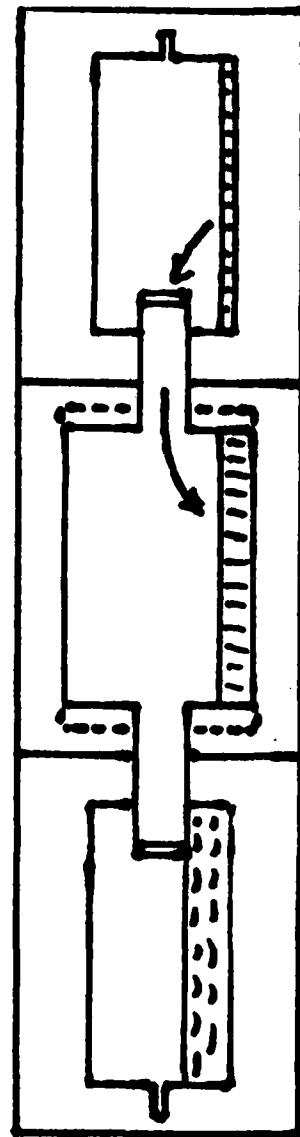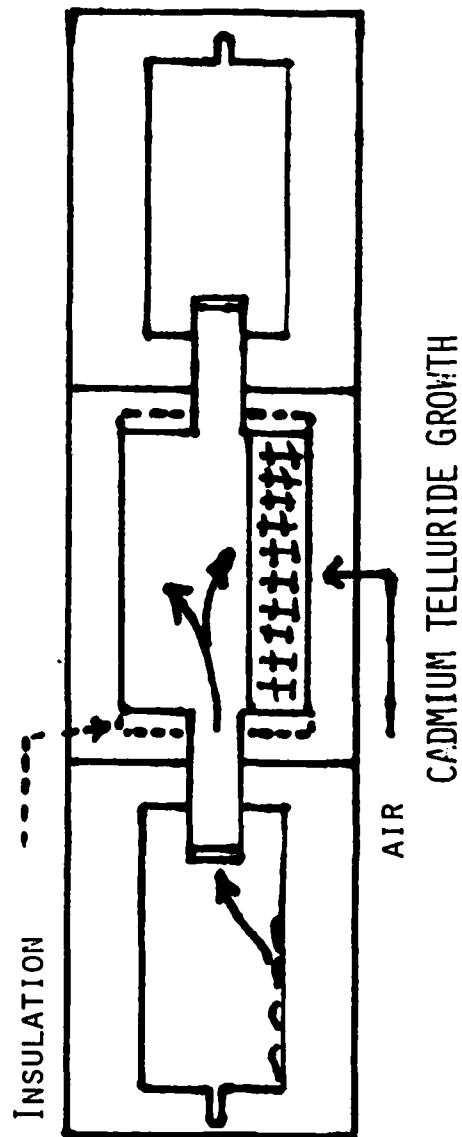
IV. Results for the Quarter

A. General

Previous reports have pointed out that program goals may
be met using a solution growth process. The problems of high
cadmium pressure are avoided by growing on the tellurium rich
side of the phase diagram. The results obtained in all solu-
tion growth attempts carried out in this program are listed
in table 1. Only runs 41-46 occurred during this quarter.

The second major conclusion reached that contributes
greatly to the potential success of this program is the se-
quence of transfer. Recognition of this fact occurred during
run 37. The process only became reproducible when we learned
that cadmium had to be transferred first. From that point on,
we were able to produce plates each run except when quartz
failures occurred.

Run No. 41, the first for this quarter, marks a return
to Cd45 Te55 solution. Also, an additional amount of material
was added to increase thickness of useful material. The re-
sulting plate of good material was only 7mm (0.3"), not any
thicker than previous runs.

Run No. 42 was a failure because the quartz tube fractured.
Run 43 was carried out in a manner similar to No. 41 but heated
to only 1060°C. Results in the literature (4) indicated our
liquidus temperature was 1036°C. We lowered the temperature
to save time and to keep pressures lower. Also, the rate of
cooling was lowered to 3°C/HR. The resulting plate was excel-
lent with large grains and a thickness of 9.5mm (0.4") or almost
2Kgms of useful material.

TABLE 1. THREE CHAMBER MELT GROWTH RESULTS

RUN NO.	TYPE	SIZE	CONDITIONS	RESULTS
26	Solution	2Kgms.6"	Cd 45 Te55, 1090-800 Air 24Hrs.	Lg. Grain, 1 layer
27	"	6Kgms.8"	" "	Cd did not transfer.
28	"	" "	" "	" "
29	"	4Kgms.8"	Cd45 Te55, 1090-800, 24Hrs. Air	Most of Cd did not transfer
30	"	2.5Kgms.8"	Cd45 Te55, 1050-800, 24Hrs. Air, Cd transferred first	Small grain plate 0.3" thick
31	"	" "	Cd45 Te55, 1050-800, 24Hrs. Tellurium transferred while Cd cooled	Most of Cd did not transfer, thin plate
32	"	" "	Cd 45 Te55, 1075-800 Air,	Thin plate, most Cd did not transfer
33	"	" "	Cd45 Te55, 1075-800	Cd did not tranfer, poor quality
34	"	" "	Cd45 Te55, 1075-800 Air,	Small grain, thin plate
35	"	" "	Cd45 Te55, 1075-800	Cd did not transfer
36	"	" "	Cd transferred first, used check valve	Quartz failed
37	"	" "	Cd transferred first 1085/cooled, 6°C/HR	Good plate
38	"	" "	Same	Excellent plate
39	"	" "	Cd48 Te52, 1095, 3°C/HR	Good plate
40	"	3.3Kgms.8"	Cd42 Te58, 1050, 3°C/HR	Good plate
41	"	4.8Kgms.8"	Cd45 Te55, 1085, 5°C/HR	Good plate
43	"	" "	Cd45 Te55, 1060, 3°C/HR	Excellent plate
44	"	" "	Cd45 Te55, 1060, 3°C/HR New Furnace	Fair plate
45	"	" "	Repeat of 44	Excellent plate
46	"	7.7Kgms.10"	Cd45 Te55, 1060, 3°C/HR	Quartz failed

Run No. 44 marks the first use of the three zone furnace specially designed for our process. A photograph of the unit is shown in figure 10 A. Figure 10 B shows the three chamber system for run No. 44 loaded into the furnace. The run was a repeat of 43 only in the new furnace. A plate with small grains resulted. Some equipment malfunctioned or an error was made in the process. The resultant plate was thin, only 4mm (0.16").

Run 45 was a rerun of No. 44 in the new furnace. All process variables were checked carefully. The result was an excellent plate with very large grains, 3-6 square inches in area. Thickness was 7mm, about 1500gms of useful material. The new furnace improved quality.

Run 46 was the first attempt to prepare a 10" plate. The reactants loaded weighed 7.7Kgms. A small leak developed in the quartz prior to heating. The quartz broke during attempts to plug the leak. Neither the round 10" chamber nor the reactants were lost. The run will be repeated in a week.
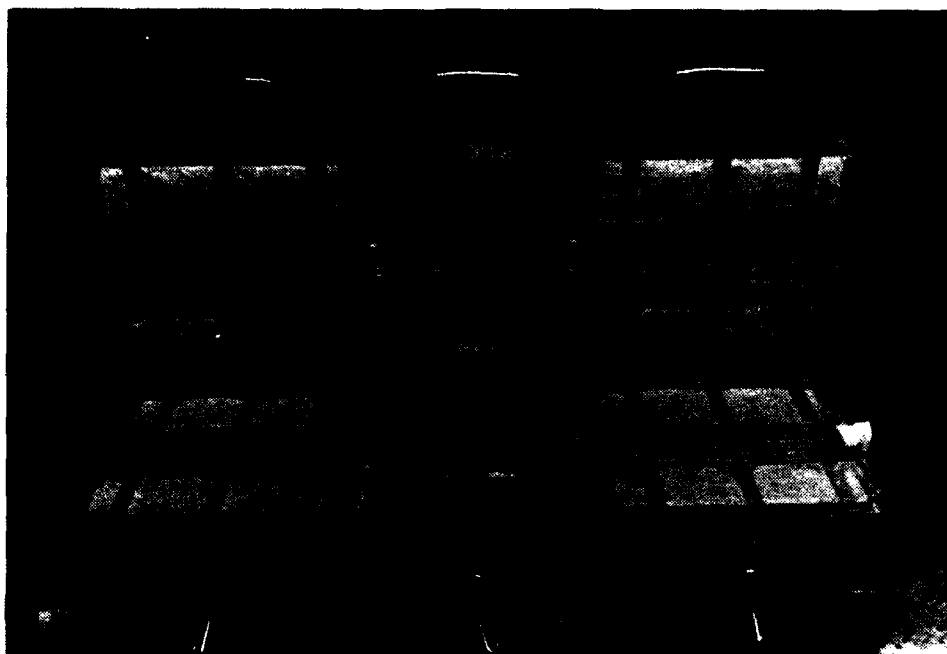
Figure 10 A
New three zone furnace

Figure 10 B
Three chamber system in place in new furnace

B. Outside Evaluation

Last quarter, large grain slices of material were turned over to several groups for evaluation. Among the groups was the Central Research Laboratories at Texas Instruments, Inc. Evaluation results were reported by Dr. Carlos Castro and Dr. Don Weirauch.

Room temperature resistivity: 2.74×10^7 ohm cm
Liquid Nitrogen resistivity: $> 10^{10}$ ohm cm
Carrier mobility (+): $51 \ cm^2$/volt sec
Carrier concentration: 4.5×10^7
Detected impurities: Cr, Mg, Si, Na, K (at < 1ppm level)
Inclusions (Te) concentration: $5.8 \times 10^6/cm^3$
Diameter of inclusions: $7 \mu m$
Infrared free carrier absorption: not detected $2-25 \mu m$

The TI results confirm the high purity and high resistivity of the material. The precipitation results indicate why the infrared bulk absorption coefficient is large. Previous attempts to remove these precipitants through vapor treatment have not been successful. More work would be needed to work out a successful procedure.

Formation of precipitants during growth of II-VI compounds is a universal problem. Only the degree and size of precipitants may be debated not their existence in cadmium telluride. Previous workers [3] had suggested that quenching would help to mininize the growth of metallic precipitates or inclusions.

C. Plate Evaluation

The decision was reached last month to apply the image spoiling test using MTF (modulation transfer function) to verify

optical homogeneity. A flat surface is required for the test
to work properly. Obtaining a flat surface is much easier on
a large diameter part (8") than on a small diameter disk (2").
For this reason, the plates were polished as flat as possible
before disks could be removed.

Amorphous Materials, Inc. uses an optical evaluation tool
called a "striaescope" to examine polished plates of AMTIR-I
glass on almost a daily basis. The system consists of a light
bulb variable aperture source placed at the focus of a 6" tel-
escope mirror. The resulting parallel light is collected by
another telescope mirror and imaged into a T.V. camera equipped
with a variable focus and a zoom lens. A part to be examined
is placed between the two mirrors in the parallel light. The
resulting image on the T.V. screen is one of transmitted near
infrared light ($\sim$1μm) through the plate covering a 6" area.
Any variation in refractive index, any inclusions or bubbles
are immediately visible.

A striaescope photograph of plate No. 41 after it has been
polished is shown in figure 11 A. Boundries between grains are
very discernible as dark lines. Dark regions indicate a high
concentration of precipitants exist. A fracture running across
the plate is visible with a little light leaking through in the
top portion.

The bottom photograph in figure 11 shows a similar photo-
graph taken of the T.V. image produced when light was trans-
mitted through plate No. 43. Note the absence of the dark
cloudy region. In run 43, quenching of the plate was used for
the first time to try to decrease precipitants. The measure
seems to have improved the quality of plates produced consider-
ably. The size of the individual grains in the plate are very

Figure 11 A
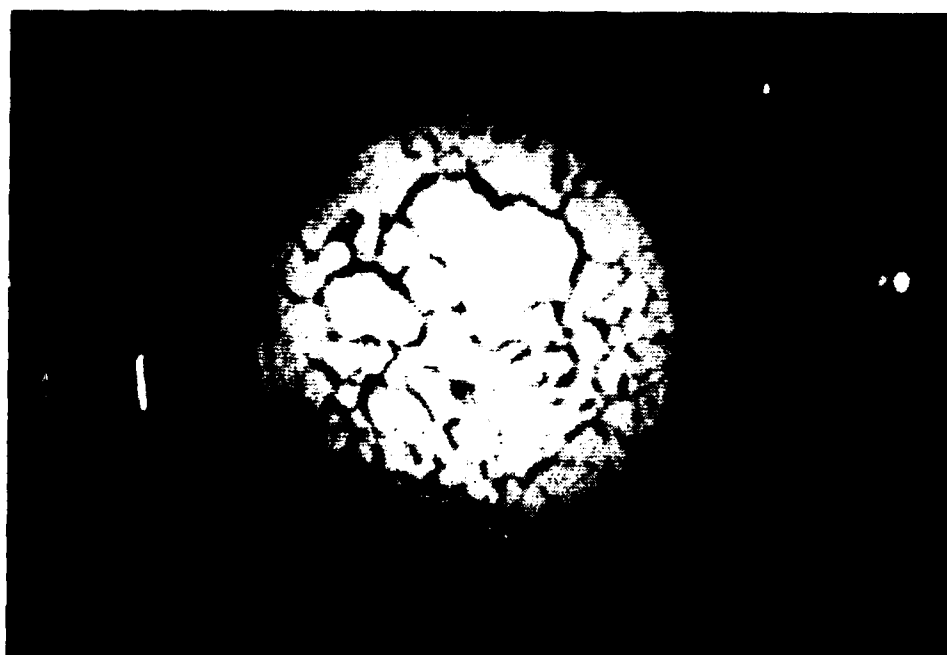Striaescope photograph of CdTe plate No. 41

Figure 11 B
Striaescope photograph of CdTe plate No. 43

apparent in the photograph. The size may be judged by remembering the full aperture is 6" in diameter. Rather large grains are apparent.

One way to verify the homogeneity of the plate is to perform the MTF image spoiling test on several regions of the plate. The procedure was used to evaluate AMTIR-I 8" and 10" diameter plates during our recent Manufacturing Methods and Technology (MM&T) program. The MTF system made by Diversified Optics uses a 4" diameter collimated 8-12μm filtered light source to perform the measurements. The reference optical module has a 2" aperture. Therefore, if the plate is positioned so that several 2" diameter regions are in the center of the optical path, the entire plate may be examined to verify optical homogeneity. A striaescope photograph in figure 12 A shows how five 2" diameter regions were marked off on the plate using a grease pencil.

The test is very sensitive to polish. Generally, for a 2" aperture, only 4 fringes of power and 1 fringe of irregularity is allowed for a test. If the polish is worse than that, the material will fail the test because of polish, not optical homogeneity.

Plates 41 and 43 were tested in this manner without success. Alignment in the optical path can also affect the results. Several attempts were made on both plates. Plate 43 scored much better than 41 which has already been indicated.

D. Disk Evaluation

All attempts to core drill 2" diameter disks from CdTe plates have not been successful. Instead, we have developed
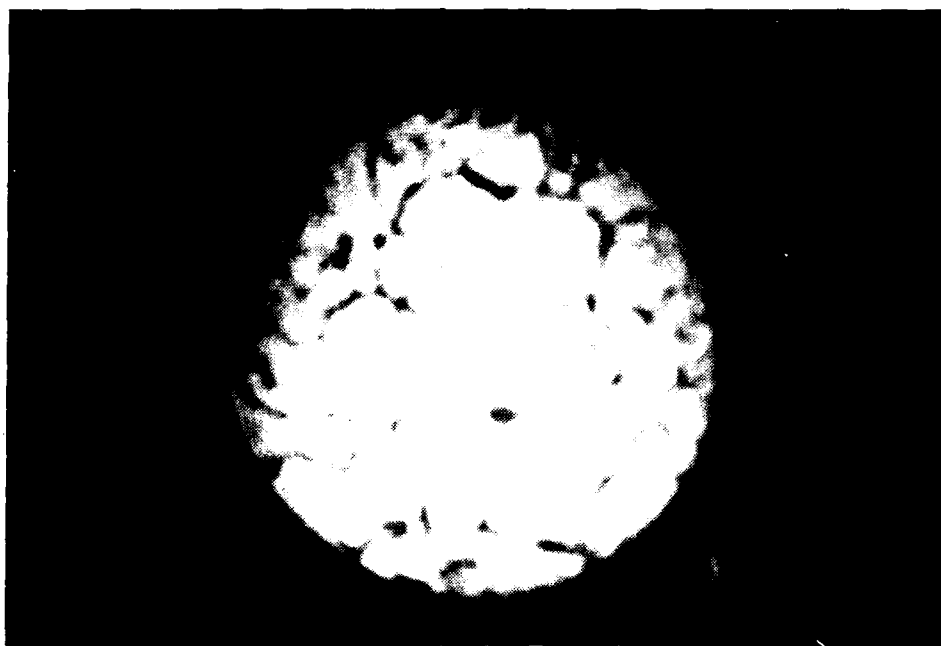
Figure 12 A
Striaescope photograph of CdTe plate No. 43 with 2" areas marked

Figure 12 B
Striaescope photograph of 2" CdTe disk cut from plate No. 41

a method in which the plate is waxed to a glass plate and sawed into 2" squares. The squares are then edged down with a diamond wheel to 2" in diameter. A striaescope photograph of one such disk cut from plate No. 41 is shown in figure 12 B. Notice the dark regions of the disk are very apparent, perhaps more than when the entire plate was evaluated. Disks 2" in diameter were fabricated from both plates 41 and 43.

The MTF test was run on the individual disks from each plate. The results are presented in table 2. A score at frequencies of 2, 10 and 20 1/mm are presented. The score is a percentage value at that frequency relative to the infrared test module evaluated without any material in the optical path. The specification set by the U. S. Army for AMTIR-I to be used in FLIR modules is 94% at 10 1/mm for a 2" aperture. The results obtained for a piece of AMTIR-I tested at the same time are presented at the bottom of the table for reference and to verify the test system is functioning properly.

Examination of the data indicates that not one of the 2" disks passed the test. Disks from No. 43 scored much higher than those of No. 41. All but one from 43 scored 80-90 at 10 1/mm in contrast to only one score of 80 for No. 41. However, examination of the polish of the surfaces tells the story. The existence of many fringes of power (FR.) and many fringes of irregularity (IRR.) absolutely rules out any chance of passing the test. Notice the AMTIR-I piece had only 1 fringe of power and 1.5 of irregularity. Also, there were opaque areas in No.41.

The inability to polish the cadmium telluride flat is thought to be caused by the dark boundry regions between the grains. One could argue that these boundries are really entrapped tellurium rich solution. The existence of a region of

TABLE 2 CdTe 2" DISK EVALUATION RESULTS

Sample No.	MTF 2 1/mm	MTF 10 1/mm	MTF 20 1/mm	POLISH FR.	POLISH IRR.	IR TRAN 2.5-20	OPTICAL EXAM
41-1	86	42	18	13	8	52-50	Several Boundries
2	89	50	17	8	8	52-51	Opaque Area, Boundries
3	91	75	60	4	12	52-50	Light Boundries
4	88	64	38	-	8	53-50	Light Boundries
5	84	45	26	-	10	53-50	Opaque Area
6	85	80	57	7	8	52-50	Opaque Area
						(7mm)	
43-1	89	83	74	-	4	48-42	Light Boundries
?	88	59	29	-	7	47-41	Light Boundries
3	89	81	68	3	5	47-41	Light Boundries
4	90	80	60	-	8	47-41	Dark Boundries
5	92	88	85	5	6	47-41	Dark Boundries
						(9mm)	
AMTIR	95	97	95	1	1.5		Clear

different material complicates the process of polishing a flat surface. Without a flat, regular surface, the MTF test results are not valid as far as optical homogeneity is concerned. For this reason, the striaescope examination of polished plates and disks has always been a much more useful homogeneity tool at Amorphous Materials than the MTF system.

The infrared transmission of each disk is also included in table 2. Disks from plate 41 show practically no wavelength decrease in transimssion 2.5-20μm. About 6% decrease is noticed for plate 43. Notice that all blanks transmit about the same amount indicating uniformity of the material. The bulk absorption for No. 41 and No. 43 is about the same, $0.17cm^{-1}$ which agrees with our previous results. Again, the separation of surface losses from bulk absorption has not taken place. Very low absorption material will require heat treating.

E. Discussion of Results

The process to make large diameter large grain plates of cadmium telluride has been developed. Application to 10" diameter chambers should present no real problem other than quartz fabrication. However, the growth of useful material appears limited to about 0.5" or less.

The quality of the material appears sufficient for use as substrates for mercury-cadmium-telluride growth. A practical method for generating 2" or other size disks has been developed. A Laser Technology wire saw as been bought and is being outfitted to cut thin slices from the disks. We are ready to furnish 2" or larger substrates for detector material growth.

Ten 2" diameter disks cut from plates 41 and 43 were submitted to DARPA and NVL for evaluation and use. The samples

were sent after evalution and represent the ones reported in the last section.

All results indicate we can not achieve our goal of growing HgCdTe layers on the 8" diameter or 10" diameter plates insitu. The material on the top of the plate is of such poor quality that introducing mercury would not lead to any useful results. Growth must occur after the good material is exposed. Probably, a second operation carried out on one or more thin disks cut from the plates would be more satisfactory. Solution growth may be used. At the same time, thin substrate evaluation results from other workers will be most helpful in supplying data comparing our material to other substrate sources.

V. Plans for Next Quarter

1. Prepare one or two 10" diameter plates and evaluate the material.

2. Devise a method to grow HgCdTe layers on material cut from our plates.

3. Make large area, large grain thin substrates available to workers in other groups involved in HgCdTe growth.

4. Devise a method for vapor treating our material to lower infrared absorption coefficient values.

5. Prepare a lens which may be tested by our MTF system.

6. Continue to try to improve material quality.

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